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HEAT-SEALABLE LACTIC ACID POLYMER LAMINATE  
[Netsu Yuchaku Kanona Nyusankei Porima Sekisotai]

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TITLE (54): HEAT-SEALABLE LACTIC ACID  
POLYMER LAMINATE

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[Claim 1] A heat-sealable lactic acid polymer laminate comprising a base layer (I) composed of a crystallized lactic acid polymer (A) and a sealing layer (II) composed of an amorphous lactic acid polymer (B) that has a softening point that is lower than the melting point of the lactic acid polymer (A).

[Claim 2] The lactic acid polymer laminate as stated in Claim 1, wherein the lactic acid polymer (A) is a lactic acid polymer having a melting point of 120 °C or higher.

[Claim 3] The lactic acid polymer laminate as stated in Claim 2, wherein the lactic acid polymer (A) is a lactic acid polymer containing from 3 to 60 % by weight of a polyester structural unit formed by dehydrating/condensing a dicarboxylic acid and a diol and/or a polyether structural unit formed by dehydrating/condensing a dicarboxylic acid and a polyether polyol.

[Claim 4] The lactic acid polymer laminate as stated in Claim 2 or 3, wherein the lactic acid polymer (A) is a lactic acid polymer having a lactic acid content of 40 % or more.

[Claim 5] The lactic acid polymer laminate as stated in Claim 2, wherein the lactic acid polymer (A) is polylactic acid.

[Claim 6] The lactic acid polymer laminate as stated in any one of Claims 1 through 5, wherein the lactic acid polymer (A) and/or the lactic acid polymer (B) comprise polymers whose polymerization

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\* Numbers in the margin indicate pagination in the foreign text.

catalysts have been deactivated by deactivators of their polymerization catalysts.

[Claim 7] The lactic acid polymer laminate as stated in any one of Claims 1 through 6, wherein the lactic acid polymer (B) is a lactic acid polymer having a softening point of from 40 to 110 °C.

[Claim 8] The lactic acid polymer laminate as stated in any one of Claims 1 through 7, wherein the base layer (I) composed of the lactic acid polymer (A) has been crystallized by thermosetting.

[Claim 9] The lactic acid polymer laminate as stated in any one of Claims 1 through 8, wherein the base layer (I) composed of the lactic acid polymer (A) has been oriented by stretching at a draw ratio of from 1.4 to 16 in terms of area.

[Claim 10] The lactic acid polymer laminate as stated in any one of Claims 1 through 9 that has a minimum storage modulus (E') of from 400 to 40,000 kg/cm<sup>2</sup> at a temperature that is 20 °C lower than its melting point, as measured by a method for testing the temperature dependency of dynamic viscoelasticity (JIS-K-7198 Method A).

[Claim 11] A film or sheet comprising the lactic acid polymer laminate stated in any one of Claims 1 through 10.

[Claim 12] A packaging container comprising the lactic acid polymer laminate stated in any one of Claims 1 through 10.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention pertains to lactic acid polymer laminates that have excellent heat-sealing properties, heat resistance, and biodegradability; lactic acid polymer laminates that are formed by heat-sealing these laminates and that are suitable for packaging or storing various foodstuffs, beverages, drugs, sundry articles, and so forth; and packaging containers, such as packaging bags, cases, and lightweight containers formed by thermoforming these laminates.

[0002]

[Related Art] Recent years have seen the use of plastics in extraordinary amounts, and their waste has caused global environmental problems, such as shortage of landfill sites, impairment of scenery, threats to marine organisms, environmental pollution, and so forth. So-called commodity resins, which are plastics that are used commonly, include polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, and the like. These resins are disposed of by incineration or by being placed in a landfill.

[0003] However, these disposal methods pose problems. For instance, incinerating such resins as polyethylene, polypropylene, polystyrene, and the like tends to cause damage to incinerators and shorten their operating life due to the high heat generated when these resins are burned. On the other hand, polyvinyl chloride produces less heat, but it is known to release a harmful gas when burned. When placed in a landfill, these commodity resins are known to remain

semipermanently, keeping their original shapes without degrading, owing to their high chemical stability, thus contributing to the serious shortage of landfill sites.

[0004] When these resins are carelessly discarded in nature, they become a factor for environmental destruction by, for example, damaging scenery because of their stability or by being mistakenly eaten by marine life, birds, and so forth and thereby reducing valuable biological resources. To solve these problems, there has been an increase in research on biodegradable polymers in recent years. As one type of resin among biodegradable polymers that have been attracting attention, there are polylactic acid and copolymers thereof, which are referred to as lactic acid polymers. These lactic acid polymers, unlike common plastics, easily degrade completely and become water and carbon dioxide eventually.

[0005] Further, because these lactic acid polymers generate low heat when burned, they do not cause incinerator damage when they are incinerated, and they also have the advantage of generating no harmful gas when burned. Because, as the starting materials, they can use plant matter that can be easily regenerated, it becomes possible to break away from use of petroleum resources that are becoming scarce. Owing to these advantages, lactic acid polymers are considered promising as replacements for commodity resins.

[0006] Heretofore, films and sheets produced by processing paper and synthetic resins as well as aluminum foil and so forth have been

used as packaging or storage materials for various foodstuffs, beverages, drugs, sundry articles, and so forth in liquid, powder, and solid forms. Films and sheets, in particular, have a number of favorable characteristics with respect to water resistance, transparency, strength, thermoforming properties, cost, and so forth and, therefore, are used in a variety of applications as packaging- or storage-use bags, cases, or thermoformed lightweight containers. For these packaging or storage materials, good heat-sealing properties and high heat resistance are particularly critical requirements.

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[0007] Films and sheets comprised of synthetic resins are processed into various bags and cases by folding them and adhering at least one side thereof by making use of the heat-sealing properties of the resins. Further, films and sheets are formed into lightweight containers, in which foodstuffs, beverages, drugs, sundry articles, and so forth are held with the use of the rigidity of the containers, by various thermoforming methods, such as vacuum forming, vacuum pressure forming, hot plate pressure forming, and deep drawing vacuum forming.

[0008] After these containers are filled, their openings are often sealed by adhering films, sheets, or matching lids that are formed by thermoforming these films or sheets. Heat sealing is also used for this purpose. As seen in the foregoing, synthetic resin films and sheets are processed in various ways by taking advantage of the heat-sealing properties thereof and put into practical use. In these

cases, the adhesion strength and appearance of the heat-sealed parts are critical characteristics.

[0009] When heat resistance during storage and transportation is taken into consideration, these containers, films, and sheets are usually required to have a heat resistance of 60 °C or higher. Lightweight containers for packing heated contents, such as freshly cooked food and so forth (for example, handy food packs for cooked rice, fried foods, and the like; prepared meal containers; hot-fill containers for jam, pudding, jelly, and the like) should be resistant to high temperatures of 80 °C or higher and are further required to have heat sealability in order to seal these containers after the containers are filled.

[0010] To meet these requirements related to heat resistance, U.S. Pat. No. 5,076,983 discloses a method for elevating heat resistance that comprises thermosetting a polylactic-acid stretched film at 130 °C for 1 minute to reduce its degree of shrinkage from 66 % to 4 %, as measured by a heating test in boiling water for 1 minute. However, this method has a problem in that this film is already crystallized and cannot be heat-sealed.

[0011]

[Problems that the Invention Intends to Solve] The objective of the present invention is to provide lactic acid polymer laminates that have a heat resistance of 60 °C or higher, high sealing strength, and

good biodegradability and that are useful for various films, sheets, packaging containers, etc.

[0012]

[Means For Solving The Problems] To achieve the aforesaid objective, the present inventors conducted extensive studies and, as a result, found out that resin laminates that are heat-sealable and that have good heat resistance can be provided with the use of lactic acid polymer laminates comprising a base layer (I) composed of a crystallized lactic acid polymer (A) and a sealing layer (II) composed of an amorphous lactic acid polymer (B) that has a softening point that is lower than the melting point of the lactic acid polymer (A). Based on this finding, the present invention was completed.

[0013] Namely, the present invention encompasses: (1) a lactic acid polymer laminate comprising a base layer (I) composed of a crystallized lactic acid polymer (A) and a sealing layer (II) composed of an amorphous lactic acid polymer (B) that has a softening point that is lower than the melting point of the lactic acid polymer (A); (2) the lactic acid polymer laminate as stated in item 1, wherein lactic acid polymer (A) is a lactic acid polymer having a melting point of 120 °C or higher;

[0014] (3) the lactic acid polymer laminate as stated in item 2, wherein the lactic acid polymer (A) is a lactic acid polymer containing from 3 to 60 % by weight of a polyester structural unit formed by dehydrating/condensing a dicarboxylic acid and a diol and/or

a polyether structural unit formed by dehydrating/condensing a dicarboxylic acid and a polyether polyol; (4) the lactic acid polymer laminate as stated in item 2 or 3, wherein the lactic acid polymer (A) is a lactic acid polymer having a lactic acid content of 40 % or more; (5) the lactic acid polymer laminate as stated in item 2, wherein the lactic acid polymer (A) is polylactic acid;

[0015] (6) the lactic acid polymer laminate as stated in any one of items 1 through 5, wherein the lactic acid polymer (A) and/or the lactic acid polymer (B) comprise polymers whose polymerization catalysts are deactivated by deactivators of their polymerization catalysts; (7) the lactic acid polymer laminate as stated in any one of items 1 through 6, wherein the lactic acid polymer (B) is a lactic acid polymer having a softening point of from 40 to 110 °C;

[0016] (8) the lactic acid polymer laminate as stated in any one of items 1 through 7, wherein the base layer (I) composed of the lactic acid polymer (A) has been crystallized by thermosetting; (9) the lactic acid polymer laminate as stated in any one of items 1 through 8, wherein the base layer (I) composed of the lactic acid polymer (A) has been oriented by stretching at a draw ratio of from 1.4 to 16 in terms of area; (10) the lactic acid polymer laminate as stated in any one of items 1 through 9 that has a minimum storage modulus (E') of from 400 to 40,000 kg/cm<sup>2</sup> at a temperature that is 20 °C lower than its melting point, as measured by a method for testing

the temperature dependency of dynamic viscoelasticity (JIS-K-7198 Method A);

[0017] (11) a film or sheet comprising the lactic acid polymer laminate stated in any one of items 1 through 10; and (12) a packaging container comprising the lactic acid polymer laminate stated in any one of items 1 through 10.

[0018]

[Preferred Mode of the Invention] The present invention provides heat-sealable lactic acid polymer laminates comprising a base layer (I) composed of a crystallized lactic acid polymer (A) and a sealing layer (II) composed of an amorphous lactic acid polymer (B) that has a softening point that is lower than the melting point of the lactic acid polymer (A); films and sheets comprising these laminates; and packaging containers, including bags and cases, that are formed by thermoforming these laminates.

[0019] The base layer (I) of the present invention that is composed of a lactic acid polymer (A) is a layer for ensuring good heat resistance, and it is composed of a crystallized lactic acid polymer. The sealing layer (II) composed of an amorphous lactic acid polymer (B) is a layer to be thermally adhered by such means as those described in the foregoing, including heat-sealing and so forth, and it is composed of an amorphous lactic acid polymer having a softening point that is lower than the melting point of the lactic acid polymer of the base layer (I). /4

[0020] The term "amorphous lactic acid polymer" as used in the present specification means a lactic acid polymer that shows no melting point peak in the method as specified in JIS-K-7121. As the lactic acid polymer (A) used for the base layer (I), the present invention uses a crystallized lactic acid polymer having a melting point of from 120 to 300 °C for the purpose of achieving good heat resistance and thermoforming properties. Lactic acid polymers that are suitable for this objective are lactic acid polymers in which the lactic acid component as a constituent of the lactic acid polymer is composed of L and D lactic-acid optical isomers preferably at a ratio (L/D) of from 100/0 to 96 [sic]/3 or from 3/96 [sic] to 0/100.

[0021] The lactic acid polymer (A) is polylactic acid or one that contains a structural unit obtained by dehydrating/condensing lactic acid and from 3 to 60 % by weight of a polyester structural unit formed by dehydrating/condensing a dicarboxylic acid and a diol and/or a polyether structural unit formed by dehydrating/condensing a dicarboxylic acid and a polyether polyol. The weight-average molecular weight of this lactic acid polymer (A) is preferably in the range of from 10,000 to 500,000.

[0022] To achieve good heat-sealing properties, the amorphous lactic acid polymer (B) used for the sealing layer (II) is a lactic acid polymer having a softening point of from 40 to 110 °C, preferably from 40 to 100 °C. Further, this lactic acid polymer is a lactic acid polymer in which the ratio of L isomer to D isomer (L/D) of the lactic

acid component is from 95.5/4.5 to 4.5/95.5. When the balance between the heat resistance and sealing properties of the lactic acid polymer laminate is taken into consideration, the melting point of the crystallized lactic acid polymer (A) preferably differs from the softening point of the amorphous lactic acid polymer (B) by at least 20 °C.

[0023] The polymers to be used in the present invention include polylactic acid as well as lactic acid polymers containing a lactic acid component and a polyester component consisting of a dicarboxylic acid component and diol component and/or polyether polyol component and mixtures of these polymers, each containing the lactic acid component in a quantity of 40 % by weight or more. Examples of the lactic acid component include L, D, and DL-lactic acid optical isomers, while examples of the dicarboxylic acid component include those having C<sub>2-10</sub> methylene chains, such as adipic acid, sebacic acid, succinic acid, and the like.

[0024] Examples of the diol component include those having C<sub>2-6</sub> main chains, such as ethylene glycol, propylene glycol, butylene glycol, 1,4-butanediol, 1,6-hexanediol, and so forth. Examples of the polyether polyol include polyethylene glycol, polypropylene glycol, polybutylene glycol, and so forth. Of these, it is ideal to use adipic acid or sebacic acid as the dicarboxylic acid component, propylene glycol as the diol component, and polypropylene glycol as the polyether polyol.

[0025] A widely practiced method for producing polylactic acid comprises synthesizing lactide, a cyclic dimer, from lactic acid and then obtaining polylactic acid having a high molecular weight by ring-opening polymerization, but the present invention may also use another method that synthesizes polylactic acid directly from lactic acid by means of dehydration/condensation. The lactic acid polymers, which are copolymers, are obtained by adding one or more kinds of accessory components, such as aliphatic polyester, aromatic polyester, caprolactone, vinyl acetate, ethylene terephthalate polymer, ethylene vinyl alcohol, and the like, during the step of the polymerization of polylactic acid or immediately thereafter and then further proceeding with the polymerization.

[0026] Furthermore, at any stage of these polymerization processes, molecular-weight increasing agents, such as polyvalent carboxylic acids and/or acid anhydrides thereof, polyvalent isocyanates, and so forth may be added so as to further elevate the molecular weight of the resulting lactic acid polymer. Examples of the polyvalent carboxylic acids include trimellitic acid and pyromellitic acid. Examples of the acid anhydrides include succinic anhydride, trimellitic anhydride, pyromellitic anhydride, and so forth. Examples of the polyvalent isocyanates include 2,4-tolylene diisocyanate, a mixture of 2,4-tolylene diisocyanate and 2,6-tolylene diisocyanate,

[0027] diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, xylylene diisocyanate, xylylene diisocyanate hydride, hexamethylene

diisocyanate, isophorone diisocyanate, triphenylmethane-4,4',4"-triisocyanate, and so forth. It is sufficient to add such a molecular-weight increasing agent in a quantity of from 0.01 to 5 % by weight of the lactic acid polymer, and, with this, the weight-average molecular weight of the lactic acid polymers, which usually reaches about 300,000 at the most, can be elevated to from about 600,000 to about 700,000.

[0028] Furthermore, the heat stability and storage stability of the polymers can be improved by adding chelating agents and acidic phosphates as a polymerization catalyst deactivator during and/or after the polymerization of these polymers. The chelating agents can minimize the cleavage of the polymer chains. The present invention may use a mixture of organic chelating agents and inorganic chelating agents.

[0029] The acidic phosphates can enhance the stability through the following mechanism: the acidic phosphates form a complex together with a metal ion in a catalyst that is contained in a composition consisting of a polyhydroxycarboxylic acid, a polyester composed of a dicarboxylic acid component and a diol component, and a molecular-weight increasing agent, thereby deactivating the catalyst and greatly improving the heat stability and storage stability of the composition.

[0030] The chelating agents used in the present invention include organic chelating agents and inorganic chelating agents. Examples of

the organic chelating agents include, but are not limited to, amino acids, phenols, hydroxycarboxylic acids, diketones, amines, oximes, phenanthrolines, pyridine compounds, dithio compounds, phenols containing N as the ligand atom, carboxylic acids containing N as the ligand atom, diazo compounds, thiols, porphyrins, and so forth.

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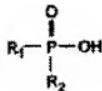
[0031] These chelating agents form a complex together with a metal ion in a catalyst contained in a hydroxycarboxylic acid polyester composition, thereby deactivating the catalyst. Inorganic chelating agents should be handled with care since they are highly hygroscopic and lose their effects after absorbing moisture. Concrete examples of the inorganic chelating agents include phosphoric acid, phosphorous acid, pyrophosphoric acid, polyphosphoric acid, and the like.

[0032] The amount of such an organic or inorganic chelating agent to be added varies depending on the type thereof and the type and amount of the catalyst contained in the polyhydroxycarboxylic acid and the polyester composed of a dicarboxylic acid component and a diol component. In general, it is preferable to add such a chelating agent in an amount of from 0.001 to 5 parts by weight, based on the total amount of the polyhydroxycarboxylic acid and the polyester composed of a dicarboxylic acid component and a diol component, or from 0.1 to 100 parts by weight per one part by weight of the catalyst employed.

[0033] The term "acidic phosphates" means acidic phosphate, phosphonate, alkylphosphonic acid, and so forth as well as mixtures thereof, and they are represented by the following general formula:

[0034]

[Chem. 1]



[0035] (wherein R<sub>1</sub> represents an alkyl group or an alkoxy group, and R<sub>2</sub> represents an alkyl group, an alkoxy group, or a hydroxyl group.)

Among these acidic phosphates, acidic phosphate is particularly effective in deactivating a catalyst. The amount of the acidic phosphates to be added varies depending on the type thereof, the type of the catalyst employed, and the kneading conditions. In general, it is preferable to add such a phosphate in an amount of from 0.001 to 5 parts by weight, based on the total amount of the polyhydroxycarboxylic acid and the polyester composed of a dicarboxylic acid component and a diol component, or from 0.1 to 100 parts by weight per one part by weight of the catalyst employed.

[0036] As the lactic acid polymers to be used in the present invention, it is especially desirable to use lactic acid polymers obtained by deactivating their polymerization catalysts with polymerization catalyst deactivators after the polymerization of the lactic acid polymers. This deactivation process of the polymerization

catalysts reduces residual monomers and oligomers, thereby contributing to the improvement of the heat-sealing properties.

[0037] The term "laminate" as used in the present specification means an object in the form of a plate having a thickness of 5,000 µm or less. The lactic acid polymer laminates of the present invention may further optionally contain, as the second and third components, other polymers and additives, such as plasticizers, stabilizers, antioxidants, anti-blocking agents, anti-fogging agents, and coloring agents. The polymers here may include aliphatic polyesters, polyvinyl alcohol, polyhydroxybutyrate-hydroxyvalerate, starch polymers, and so forth.

[0038] As the additives, the present invention may use polyester-type plasticizers comprised of, for example, 1,3-butanediol and adipic acid; plasticizers, such as dioctyl phthalate, polyethylene glycol adipate, and so forth; stabilizers, such as epoxidized soybean oil, carbodiimide, and the like; antioxidants, such as 2,6-di-tert-butyl-4-methylphenol (BHT), butyl hydroxyanisole (BHA), and the like; anti-blocking agents, such as silica, talc, and the like; anti-fogging agents, such as glycerol fatty acid esters, monostearyl citrate, and the like; coloring agents, such as titanium oxide, carbon black, ultramarine, and the like; and so forth.

[0039] Examples of the adhesion method that utilizes thermal adhesion include heat-sealing, impulse sealing, fuse sealing, impulse fuse sealing, ultrasonic sealing, high-frequency sealing, and so forth,

of which heat-sealing, impulse sealing, and fuse sealing are more commonly employed in the art. The lactic acid polymer laminate of the present invention is prepared by laminating the base layer (I) and the sealing layer (II). The most practical lamination method here is the coextrusion film-forming method with the use of two or more extruders. Alternatively, the present invention may use a method in which the sealing layer (II) is laminated by melt extrusion on the base layer (I), which has been formed into a film beforehand, or another method in which the base layer (I) and sealing layer (II), which have been formed into films beforehand, are laminated by means of an adhesive.

[0040] The base layer (I) may optionally be metallized with a metal or a metal oxide or printed. It may have two or more of these treatments performed on it. The thickness of the base layer (I) is preferably in the range of from 5 to 3,000  $\mu\text{m}$ , but, when strength and cost efficiency are taken into consideration, the range of 5 to 200  $\mu\text{m}$  is more desirable. It is further preferable that the base layer (I) has such a thickness as to be called "a film", that is, a thickness of 100  $\mu\text{m}$  or less, namely, from 5 to 100 .

[0041] The term "sheet" as used herein means one having a thickness that exceeds 100  $\mu\text{m}$  but not 3,000  $\mu\text{m}$ . From the viewpoint of the film-forming properties, the thickness of the sealing layer (II) preferably ranges from 1 to 30  $\mu\text{m}$ , but, when seal thinning and cost efficiency are taken into consideration, the thickness of the sealing layer preferably ranges from 2 to 20  $\mu\text{m}$ , better yet, from 3 to 10  $\mu\text{m}$ .

[0042] The following will describe the method for forming lactic acid polymer films by extrusion and the conditions therefor. Since lactic acid polymers are highly hygroscopic and hydrolyzable, the moisture conditions should be strictly regulated. When a lactic acid polymer film is formed with a commonly employed single screw extruder, the polymer should be dehydrated and dried with a vacuum drier or the like prior to the film formation. By using a vent-type twin screw extruder, a high dehydration effect can be achieved, and, therefore, the drying step can be omitted, which enables efficient film formation.

[0043] The melt-extrusion temperature in forming the lactic acid polymer films is usually in the range of from 150 to 250 °C, though the present invention is not restricted thereto. The melt-extruded sheet is cast so as to have a predetermined thickness and, if necessary, cooled. In this step, a touch roll or an air knife is used /6 if the sheet is too thick, and electrostatic pinning is used if it is too thin, thus forming a sheet having a uniform thickness. In the melt extrusion, lips are positioned at intervals of from 0.2 to 3.0 mm, preferably from 0.2 to 1.5 mm from the viewpoint of film-forming properties.

[0044] Next, the lamination methods will be described in detail. To produce a lactic acid polymer laminate by the coextrusion film-forming method, first, the base layer (I) and the sealing layer (II) are melted and kneaded with separate extruders and then laminated in a T-die or a feed block located before it, and the laminate thus formed

is passed through the T-die to form a film. The extrusion film-forming method and its conditions are basically the same as those described in the foregoing.

[0045] When the base layer (I) does not adhere well to the sealing layer (II), it is required to put an adhesive layer (III) between them. As the resin used here, the present invention preferably uses copolymers obtained by introducing special functional groups into polyolefins or the like, butene-based copolymers, polyethylene imine, modified cellulose, and so forth. The thickness of the adhesive layer (III) is preferably in the range of from 0.5 to 20  $\mu\text{m}$ .

[0046] Melt extrusion lamination is a method that adheres, with a laminator, the base layer (I) that is supplied from a feeder and the sealing layer (II) that is introduced from an extruder into a T-die for laminator use, thereby forming a laminate. The extrusion film formation of the sealing layer (II) is performed basically in the same manner and under the same conditions as those described in the foregoing. When the base layer (I) does not adhere well to the sealing layer (II), the base layer (I) is subjected, prior to feeding it into the laminator, to a corona discharge treatment, flame plasma treatment, chemical etching treatment with chromic acid or the like, surface treatment with ozone, UV light, or the like, or surface roughening treatment, such as sandblasting or the like, to improve the adhesion. Alternatively, an appropriate anchor coating is employed so as to improve the adhesion.

[0047] Methods that laminate the base layer (I) and the sealing layer (II) that are formed in advance include wet lamination, dry lamination, and so forth. In these methods, an adhesive needs to be applied onto the base layer (I) or the sealing layer (II) before laminating them. Examples of the adhesive usable in the wet lamination include adhesives based on proteins, such as casein, gelatin, and the like; those based on carbohydrates, such as starches, cellulose derivatives, and the like; and those based on synthetic resins, such as vinyl acetate, acrylates, acryl-modified vinyl acetate, ethylene-vinyl acetate copolymer resin, and the like.

[0048] Examples of the adhesive usable in the dry lamination include single-component urethane adhesives, such as polyether polyurethane polyisocyanate, polyester polyurethane polyisocyanate, and the like, which have isocyanate groups introduced into the terminals thereof, and two-component urethane adhesives consisting of the main component having hydroxyl groups, such as polyester resins (polyester polyol, polyester polyurethane polyol, etc.) or polyether resins (polyether polyurethane polyol, etc.), and of a hardener having isocyanate groups, said two components being mixed before use. These adhesives are preferably applied at a rate of from about 1 to 5 g/m<sup>2</sup>.

[0049] The term "heat resistance" as used in the present specification means practical heat resistance that, at a processing temperature or in use, allows a film, a sheet, or a processed product thereof to sustain certain elasticity and thus prevents appearance

damage and deformation. Films, sheets, or processed products thereof, such as bags, cases, lightweight containers, and the like, are usually kept in sealed conditions inside transportation containers, warehouses, and the like even during ordinary transportation or storage, and, if no air-conditioning is provided, these articles are often exposed to a high environmental temperature of 50 °C or higher in summer. Therefore, these articles are required to have a heat resistance of 60 °C or higher for practical purposes.

[0050] To impart heat resistance, the lactic acid polymer (A) used for the lactic acid polymer base layer (I) is crystallized, and, as the method for thermally treating the lactic acid polymer for this purpose, thermosetting will be described in the following. Thermosetting may be conducted on either the base layer (I) alone for which the lactic acid polymer (A) is used or on a laminate of the base layer (I) and the sealing layer (II).

[0051] Although the thermosetting temperature and time are not particularly limited, it is preferable, for the purpose of establishing an adequate crystallization speed, to set the heating temperature within the range of from a temperature that is 40 °C lower than the crystallization temperature (Tc) of the lactic acid polymer (A) to the melting point (Tm) thereof. To achieve a good surface condition and high heat resistance, it is particularly desirable that the thermosetting temperature falls within the range of the

crystallization temperature ( $T_c$ ) to a temperature that is 40 °C higher than that temperature.

[0052] Implementing stretching prior to or simultaneously with the thermosetting accelerates the crystallization, thereby making it possible to improve the heat resistance within a short heating time of 5 to 30 seconds. Furthermore, since the crystallization proceeds in association with crystal orientation in this case, the lactic acid polymer can achieve improved heat resistance while retaining its high transparency.

[0053] This stretching is carried out by calendaring, longitudinal uniaxial stretching, transversal uniaxial stretching, simultaneous biaxial stretching, or consecutive biaxial stretching of a sheet that has been just formed by melt-extrusion of the lactic acid polymer or that has been stored, though the present invention is not restricted thereto. This stretching process may be conducted on either the base layer (I) alone for which the lactic acid polymer (A) is used or on a laminate of the base layer (I) and the sealing layer (II).

[0054] The heating temperature in this step is preferably in the range of from the glass transition temperature ( $T_g$ ) of the base layer (I) to the melting point thereof, better yet, from the glass transition temperature to a temperature that is 50 °C higher than the glass transition temperature ( $T_g$ ). However, a temperature that is 10 to 40 °C higher than the glass transition temperature ( $T_g$ ) of the base layer (I) is the most desirable since the resulting sheet has a good

surface condition. With respect to the draw ratio, a draw ratio in the range of from 1.4 to 16, in terms of area ratio, ensures a good surface condition and high transparency, but the range of from 2 to 16 is more desirable.

[0055] The thermosetting may be performed by heating the polymer for a given period of time in a forced air circulation or with the use of radiant heat from an infrared heater or the like or by bringing the polymer into contact with a hot plate, mold, or roll for a certain period of time and thus heating the polymer. High productivity can be achieved by using an apparatus called a tenter, with which a sheet or a film can be continuously thermoset in forced air circulation under /7 heating. Since this apparatus is designed for stretching, it can complete stretching and thermosetting within a short period of time, thus yielding high productivity. Thus, the lactic acid polymer laminate can be efficiently crystallized.

[0056] When the lactic acid polymer laminate is formed into lightweight containers, in which foodstuffs, beverages, drugs, sundry articles, and so forth are packaged by making use of the rigidity of the containers, by various thermoforming methods, such as vacuum forming, vacuum pressure forming, hot plate pressure forming, deep drawing vacuum forming, and the like, it is recommended to perform the thermosetting on the mold used for the thermoforming. The thermosetting conditions in this case, that is, the mold temperature

and time, are not specifically limited but are usually selected from the thermosetting temperatures specified in the foregoing.

[0057] The lactic acid polymer laminate of the present invention has a heat resistance of 60 °C or above, which is a sufficient level for everyday household use, and it has a minimum storage modulus (E') of 400 kgf/cm<sup>2</sup> or larger at a temperature that is 20 °C lower than the melting point of the lactic acid polymer (A), as measured by a method for testing the temperature dependency of dynamic viscoelasticity (JIS-K-7198 Method A).

[0058] When the storage modulus (E') is smaller than 400 kgf/cm<sup>2</sup>, good elasticity cannot be achieved at 50 to 60 °C; as a result, a container made of such a laminate cannot support the content and undergoes deformation due to the weight of the content therein. When flexibility in use at ordinary temperature is also taken into consideration, it is preferable to adjust the storage modulus (E') within the range up to 40,000 kgf/cm<sup>2</sup>. Furthermore, to achieve a high heat resistance of 80 °C or above, it is more desirable to set the storage modulus (E') to 900 kgf/cm<sup>2</sup> or higher.

[0059] The test of this temperature dependency of dynamic viscoelasticity is carried out at a temperature increase rate of 2 °C/minute. The glass transition temperature (Tg), crystallization temperature (Tc), and melting point (Tm) as used in the present specification are respectively the T<sub>g</sub>, T<sub>pc</sub>, and T<sub>pm</sub> as specified in JIS-K-7121, which are determined at a temperature increase rate of 10

°C/minute. The term "amorphous lactic acid polymer" as used in the present specification means a lactic acid polymer that shows no melting point peak when tested by the method as specified in JIS-K-7121. The softening point is measured in accordance with JIS-K-7206 Method A.

[0060] The heat-sealable lactic acid polymer laminate of the present invention, which has a base layer (I) composed of a lactic acid polymer (A) and a sealing layer (II) composed of an amorphous lactic acid polymer (B) that has a softening point that is lower than the melting point of the lactic acid polymer (A), can exhibit a high sealing strength when two sealing layers (II) serve as the sealing faces, but it can also yield an effective sealing strength when the base layer (I) and the sealing layer (II) serve as the sealing faces.

[0061] The heat-sealable lactic acid polymer laminate of the present invention can be used for packaging containers that are required to have heat resistance for everyday use. In particular, the laminate is suitable for producing packaging bags, cases, and thermoformed lightweight containers for packaging or storage use.

[0062] The term "packaging bags" as used herein means commonly used bags, and they are made of synthetic resin films by folding them or by sealing them by means of adhesion, etc., and have a two-dimensional structure or, in some cases, a three-dimensional structure. The articles to be packaged with these bags include foodstuffs, such as vegetables, confectionery, bread, and so forth; sundry articles;

rice; fertilizers; and so forth. The lactic acid polymer laminate obtained in the present invention can be used as folded or heat-sealed bags in these applications.

[0063] The term "cases" as used herein means three-dimensional packaging materials that are produced, without the use of thermoforming, such as vacuum forming or vacuum pressure forming, by three-dimensionally processing sheets into boxes by folding them or into cylinders without folding them and optionally bonding the ends by heat-sealing or the like. These cases are employed for packaging cosmetics, stationery, small electrical appliances, toys, sundry articles, and so forth.

[0064] The term "cases" also includes two-dimensional materials for packaging documents and the like, and these are formed by folding one end of a sheet and heat-sealing another end thereof or heat-sealing two ends while keeping the remaining two ends open. The lactic acid polymer laminate obtained herein can be used for these various purposes as folded or heat-sealed cases.

[0065] The term "lightweight containers" means three-dimensional packaging materials that are produced from films or sheets by a thermoforming method, such as vacuum forming, vacuum pressure forming, hot plate pressure forming, deep-drawing vacuum forming, or the like. These lightweight containers are formed in various modes, including main bodies with lids therefor, trays, food packs, blister packs, PTP packages, cups for holding liquid contents, and so forth. These

lightweight containers are used for packaging solid foodstuffs, such as vegetables, meat, prepared meals, confectionery, bread, fried food, and so forth; foodstuffs that need to be poured into containers, such as jelly, jam, pudding, and the like; milk products; beverages, such as juice and the like; drugs in the form of tablets and the like; sundry articles; and so forth.

[0066] The lactic acid polymer laminate obtained in the present invention has excellent heat sealing properties and heat resistance sufficient for everyday use and are ideal for use for packaging materials, in particular, for bags, cases, and thermoformed lightweight containers, that are intended for packaging or storing various food products, beverages, drugs, sundry articles, and so forth.

[0067]

[Working Examples] The following will explain the present invention in further detail by presenting working examples, but the present invention is not limited to or restricted by these examples. First, the methods for producing the lactic acid polymers employed in the present invention will be described.

[0068] (Preparation of lactic acid polymer A) A mixture of 98 % by mol of L-lactide and 2 % by mol of D-lactide was stirred in an inert gas atmosphere at 165 °C for 1 hour, after which 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 8 hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as

a deactivator, and the mixture was kneaded. The lactic acid polymer (A) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 192,000 (as measured by GPC), a glass transition temperature (Tg) of 56 °C, a crystallization temperature (Tc) of 110 °C, and a melting point (Tm) of 163 °C. This resin is referred to as P1.

[0069] L-Lactide was stirred in an inert gas atmosphere at 185 °C for 1 hour, after which 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 8 hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as a deactivator, and the mixture was kneaded. The lactic acid polymer (A) thus obtained was a /8 colorless and transparent resin having a weight-average molecular weight of 252,000 (as measured by GPC), a glass transition temperature (Tg) of 59 °C, a crystallization temperature (Tc) of 110 °C, and a melting point (Tm) of 176 °C. This resin is referred to as P2.

[0070] To 5 parts by weight of an aliphatic polyester [weight-average molecular weight: 24,000 (in terms of polystyrene equivalent molecular weight), 50 % by mol of sebacic acid, and 50 % by mol of propylene glycol] was added 95 parts by weight of lactide (99 % by mol of L-lactide and 1 % by mol of D-lactide). After the ambience was purged with an inert gas, the mixture was blended at 170 °C for 1 hour. Next, 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 8

hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as a deactivator, and the mixture was kneaded. The lactic acid polymer (A) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 203,000 (as measured by GPC), a glass transition temperature (Tg) of 55 °C, a crystallization temperature (Tc) of 108 °C, and a melting point (Tm) of 168 °C. This resin is referred to as P3.

[0071] To 20 parts by weight of an aliphatic polyester [weight-average molecular weight: 35,000 (in terms of polystyrene equivalent molecular weight), 50 % by mol of sebacic acid, and 50 % by mol of 1,6 hexanediol] was added 80 parts by weight of lactide (97 % by mol of L-lactide and 3 % by mol of D-lactide). After the ambience was purged with an inert gas, the mixture was blended at 170 °C for 1 hour. Next, 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 8 hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as a deactivator, and the mixture was kneaded. The lactic acid polymer (A) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 113,000 (as measured by GPC), a glass transition temperature (Tg) of 49 °C, a crystallization temperature (Tc) of 93 °C, and a melting point (Tm) of 162 °C. This resin is referred to as P4.

[0072] To 40 parts by weight of an aliphatic polyester [weight-average molecular weight: 34,000 (in terms of polystyrene equivalent

molecular weight), 50 % by mol of sebacic acid, 25 % by mol of ethylene glycol, and 25 % by mol of 1,6-hexanediol] was added 60 parts by weight of lactide (97 % by mol of L-lactide and 3 % by mol of D-lactide). After the ambience was purged with an inert gas, the mixture was blended at 165 °C for 1 hour. Next, 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 8 hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as a deactivator, and the mixture was kneaded. The lactic acid polymer (A) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 102,000 (as measured by GPC), a glass transition temperature (Tg) of 51 °C, a crystallization temperature (Tc) of 73 °C, and a melting point (Tm) of 162 °C. This resin is referred to as P5.

[0073] (Preparation of amorphous lactic acid polymer B) A mixture of 70 % by mol of L-lactide and 30 % by mol of D-lactide was stirred in an inert gas atmosphere at 165 °C for 1 hour, after which 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 8 hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as a deactivator, and the mixture was kneaded. The lactic acid polymer (B) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 272,000 (as measured

by GPC) and a glass transition temperature (Tg) of 52 °C, but it did not have a melting point (Tm). This resin is referred to as P6.

[0074] A mixture of 30% by mol of L-lactide and 70 % by mol of D-lactide was stirred in an inert gas atmosphere at 165 °C for 1 hour, after which 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 8 hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as a deactivator, and the mixture was kneaded. The lactic acid polymer (B) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 167,000 (as measured by GPC) and a glass transition temperature (Tg) of 52 °C, but it did not have a melting point (Tm). This resin is referred to as P7.

[0075] To 50 parts by weight of an aliphatic polyester [weight-average molecular weight: 75,000 (in terms of polystyrene equivalent molecular weight), 50 % by mol of sebacic acid, and 50 % by mol of ethylene glycol] was added 50 parts by weight of lactide (90 % by mol of L-lactide and 10 % by mol of D-lactide). After the ambience was purged with an inert gas, the mixture was blended at 165 °C for 1 hour. Next, 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 8 hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as a deactivator, and the mixture was kneaded. The lactic acid polymer (B) thus obtained was a colorless and

transparent resin having a weight-average molecular weight of 81,000 (as measured by GPC) and a glass transition temperature (Tg) of 46 °C, but it did not have a melting point (Tm). This resin is referred to as P8.

[0076] To 5 parts by weight of a polyester containing aromatic carboxylic acids and aliphatic dicarboxylic acids [weight-average molecular weight: 47,000 (in terms of polystyrene equivalent molecular weight), 16 % by mol of terephthalic acid, 14 % by mol of isophthalic acid, 20 % by mol of adipic acid, 23 % by mol of ethylene glycol, and 27 % by mol of neopentyl glycol] was added 95 parts by weight of lactide (95 % by mol of L-lactide and 5 % by mol of D-lactide). After the ambience was purged with an inert gas, the mixture was melted and mixed at 165 °C for 1 hour. Next, 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 6 hours. Thereafter, 0.04 part by weight of acidic phosphate was added to the reaction system as a deactivator, and the mixture was kneaded. The lactic acid polymer (B) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 195,000 (as measured by GPC) and a glass transition temperature (Tg) of 57 °C, but it did not have a melting point (Tm). This resin is referred to as P9.

[0077] A mixture of 70 % by mol of L-lactide and 30 % by mol of D-lactide was stirred in an inert gas atmosphere at 165 °C for 1 hour, after which 0.02 part by weight of tin octanoate was added thereto as

an esterifying catalyst, and the resulting mixture was reacted for 8 hours. After this, no deactivator was added. The lactic acid polymer (B) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 272,000 (as measured by GPC) and a glass transition temperature (Tg) of 52 °C, but it did not have a melting point (Tm). This resin is referred to as P10.

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[0078] To 5 parts by weight of a polyester containing aromatic carboxylic acids and aliphatic dicarboxylic acids [weight-average molecular weight: 47,000 (in terms of polystyrene equivalent molecular weight), 16 % by mol of terephthalic acid, 14 % by mol of isophthalic acid, 20 % by mol of adipic acid, 23 % by mol of ethylene glycol, and 27 % by mol of neopentyl glycol] was added 95 parts by weight of lactide (95 % by mol of L-lactide and 5 % by mol of D-lactide). After the ambience was purged with an inert gas, the mixture was melted and mixed at 165 °C for 1 hour. Next, 0.02 part by weight of tin octanoate was added thereto as an esterifying catalyst, and the resulting mixture was reacted for 6 hours. No deactivator was added. The lactic acid polymer (B) thus obtained was a colorless and transparent resin having a weight-average molecular weight of 195,000 (as measured by GPC) and a glass transition temperature (Tg) of 57 °C, but it did not have a melting point (Tm). This resin is referred to as P11.

[0079] (Working Examples 1 through 5) Using each lactic acid polymer (A) and each amorphous lactic acid polymer (B) specified in Table 1 as the base layer (I) and as the sealing layer (II),

respectively, a 35 µm-thick laminate film in which the base layer (I) was 20 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Thereafter, this film was thermoset in an air oven at 100 °C for 10 minutes. The laminate films thus obtained were evaluated as follows.

[0080] (1) Measurement of sealing strength

The sealing layers of two laminate films obtained in the aforesaid manner were put together face to face, each as a sealing face, and heat-sealed with a heat-sealer (a product of Tester Sangyo Co.) Thereafter, a 180°-angle peeling test was carried out with a tensile tester (a product of Shimadzu Corporation), and the adhesion strength of the heat-sealing formed by the heat-sealing method was measured as the sealing strength. The results are shown in Table 1.

[0081] Sealing conditions: seal bar temperature, from 60 to 140 °C; sealing pressure, 2 kgf/cm<sup>2</sup>; and sealing time, 1 second (the size of the seal bar used was 10 x 300 mm.)

Measurement of sealing strength: in accordance with JIS-Z-1707.

[0082] (2) Evaluation of heat resistance

(1) Actual use test: Each laminate film obtained in the foregoing was cut into a 20 cm square piece, and a 300 g weight was placed at the center of the test piece and then wrapped by tying the four corners of the test piece, thereby preparing a simple test bag. The test bags thus prepared were hung inside air ovens that were set at 60 °C and 80 °C test temperatures, with the connected corners facing upward. Twenty

minutes later, the effect of the weight on the film was observed. The length of each test bag when it was hung was 13.5 cm. O was assigned to a test bag that showed no noticeable change (that is, the length of the test bag was within 14 cm); X to a test bag that showed considerable elongation and deformation (that is, the length of the test bag was longer than 15 cm) or that tore, causing the weight to drop; and Δ to a test bag that was between these conditions. The results are shown in Table 1.

[0083] (2) Measurement of storage modulus (E'): In accordance with JIS-K-7198 Method A, the storage modulus (E') of each sample was measured at a temperature that was 20 °C lower than the melting point of the crystallized lactic acid polymer (A), and the minimum value was found. The results are shown in Table 1.

[0084] (3) Haze value: determined in accordance with JIS-K-7105. The results are shown in Table 1.

(4) Melting point of resin: Determined in accordance with JIS-K-7121. The results are shown in Table 1.

(5) Softening point of resin: Determined in accordance with JIS-K-7206. The results are shown in Table 1.

[0085] (6) Evaluation of biodegradability: In an outdoor compost container (capacity: 100 L), 5 kg of food scraps were placed, and a 10 cm square test piece that was cut out from each laminate film obtained in the foregoing was placed thereon. Further, additional food scraps were placed thereon to a thickness of about 5 cm, and, one month later,

the condition of the test piece was evaluated visually. Incidentally, this test was performed in summer. The evaluation criteria are as follows. O was assigned to a sample that showed considerable deterioration in properties and scarcely sustained the shape; Δ to a sample that showed deformation and clouding but sustained the shape; and X to a sample that sustained the initial condition without showing any clouding, deformation, etc.

[0086] Each of these laminate films had its sealing initiation temperature at about 80 °C and maintained a good sealing strength (1,000 gf/15 mm or above) at a temperature of 90 °C or higher. In the actual use tests performed with the use of weights, these films exhibited good heat resistance at 60 °C and 80 °C test temperatures. The minimum storage modulus (E') of each laminate film here was 900 kgf/cm<sup>2</sup> or above. Further, the lactic acid polymer laminates produced in the foregoing had excellent transparency and biodegradability.

[0087] (Working Examples 6 through 7) Using each lactic acid polymer (A) and each amorphous lactic acid polymer (B) specified in Table 1 as the base layer (I) and as the sealing layer (II), respectively, a 35 µm-thick laminate film in which the base layer (I) was 20 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Thereafter, this film was thermoset in an air oven at 100 °C for 10 minutes. The laminate film thus obtained was evaluated as follows.

[0088] (1) Measurement of sealing strength

The sealing layer and base layer of two laminate films obtained above were put together face to face, each as a sealing face, and heat-sealed with a heat-sealer (a product of Tester Sangyo Co.) Thereafter, a 180°-angle peeling test was carried out with a tensile tester (a product of Shimadzu Corporation), and the adhesion strength of the heat-sealing formed by the heat-seal method was measured as the sealing strength. The results are shown in Table 1.

[0089] Sealing conditions: seal bar temperature, from 60 to 140 °C; sealing pressure, 2 kgf/cm<sup>2</sup>; and sealing time, 1 second (the size of the seal bar used was 10 x 300 mm.)

Measurement of sealing strength: in accordance with JIS-Z-1707.

(2) Evaluation of heat resistance: according to the same method used in Working Examples 1 through 5. The results are shown in Table 1.

(3) Haze value: determined in accordance with JIS-K-7105. The results are shown in Table 1.

(4) Melting point of resin: determined in accordance with JIS-K-7121. The results are shown in Table 1.

(5) Softening point of resin: determined in accordance with JIS-K-7206./10  
The results are shown in Table 1.

[0090] (6) Biodegradability test: according to the same method used in Working Examples 1 through 5. The results are shown in Table 1.

Each of these laminate films had a sealing strength of from 160 to 180 gf/15 mm or thereabouts at a temperature of 90 °C or higher.

With respect to their heat resistance, in the actual use tests

performed with the use of weights, these films exhibited no problem at the 60 °C and 80 °C test temperatures. The minimum storage modulus ( $E'$ ) of each laminate film here was 900 kgf/cm<sup>2</sup> or above. The lactic acid polymer laminates produced in the foregoing had excellent transparency and biodegradability.

[0091] (Working Examples 8 through 9) Using each lactic acid polymer (A) and each amorphous lactic acid polymer (B) specified in Tables 1 and 2 as the base layer (I) and as the sealing layer (II), respectively, a 140 µm-thick laminate sheet in which the base layer (I) was 80 µm thick and the sealing layer (II) 60 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Next, the obtained film was stretched by using a single-engine biaxial stretching machine (a product of Iwamoto Seisakusho Co.) under the following conditions: stretching temperature, 65 °C; preheating time, 5 minutes; stretching rate, 100 %/minute; stretching ratio, 2 X 2 (length X width); and area draw ratio: 4, thereby preparing a drawn film of 35 µm in thickness. Thereafter, this film was fixed in a frame and thermoset in an air oven at 100 °C for 20 seconds.

[0092] The sealing strength of the obtained laminate films was measured. In addition, their heat resistance, haze value, and biodegradability were evaluated by the same methods as those employed in Examples 1 to 5. The results are shown in Tables 1 and 2. Each of these laminate films had its sealing initiation temperature at about 80 °C and maintained a good sealing strength (1,000 gf/15 mm or above)

at a temperature of 90 °C or higher. With respect to heat resistance, in the actual use tests performed with the use of weights, the film of Working Example 8 exhibited no problem at the 60 °C and 80 °C test temperatures. The film of Example 9 showed slight elongation at 80 °C. The minimum storage modulus (E') of the laminate film of Example 8 was 900 kgf/cm<sup>2</sup>, while that of the film of Example 9 was 600 kgf/cm<sup>2</sup>. The films obtained here had excellent transparency and biodegradability.

[0093] (Working Example 10) Using the lactic acid polymer (A) and amorphous lactic acid polymer (B) specified in Table 2 as the base layer (I) and as the sealing layer (II), respectively, two kinds of 25 µm-thick single-layer films were formed by extrusion with an extruder (a product of Tanabe Plastics Co.) Next, only the single-layer film composed of the lactic acid polymer (A) was thermoset in an air oven at 100 °C for 10 minutes. Thereafter, a 30 % solution of gelatin was applied to one surface of each of these two kinds of single-layer films, which were then adhered to each other under pressure of 2 kgf/cm<sup>2</sup> and dried. As a result, a laminate film having a good appearance was obtained. The sealing strength, heat resistance, haze value, and biodegradability of the laminate film thus obtained were evaluated by the same methods as those used in Working Examples 1 through 5. The results are shown in Table 2.

[0094] The laminate film thus prepared had its sealing initiation temperature at about 80 °C and maintained a good sealing strength (1,000 gf/15 mm or above) at a temperature of 90 °C or higher. With

respect to heat resistance, in the actual use tests performed with the use of weights, the film exhibited no problem at the 60 °C and 80 °C test temperatures. The minimum storage modulus (E') of the laminate film was higher than 900 kgf/cm<sup>2</sup>, namely, 1100 kgf/cm<sup>2</sup>. The film obtained here had excellent transparency and biodegradability.

[0095] (Working Example 11) Using the lactic acid polymer (A) and amorphous lactic acid polymer (B) specified in Table 2 as the base layer (I) and as the sealing layer (II), respectively, the sealing layer (II) (15 µm) was formed by extrusion on both surfaces of the base layer (I) with a coextruder (a product of Tanabe Plastics Co.), thereby obtaining a 50 µm-thick laminate film. Thereafter, this film was thermoset in an air oven at 100 °C for 10 minutes. The sealing strength, heat resistance, haze value, and biodegradability of the laminate film thus obtained were evaluated by the same methods as those used in Working Examples 1 through 5. The results are shown in Table 2.

[0096] Said laminate film had its sealing initiation temperature at about 80 °C and maintained a good sealing strength (1,000 gf/15 mm or above) at a temperature of 90 °C or higher. With respect to heat resistance, in the actual use tests performed with the use of weights, the film exhibited no problem at the 60 °C test temperature, but it showed elongation at 80 °C. The minimum storage modulus (E') of each [sic] laminate film here was 780 kgf/cm<sup>2</sup>. The transparency and biodegradability of the film were excellent.

[0097] (Working Example 12) Using the lactic acid polymer (A) and an amorphous lactic acid polymer (B) specified in Table 2 as the base layer (I) and as the sealing layer (II), respectively, a 35 µm-thick laminate film in which the base layer (I) was 20 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Thereafter, this film was thermoset in an air oven at 100 °C for 10 minutes. Then, one end of the laminate film thus obtained was folded to form the bottom portion of a packaging bag, with the sealing layer disposed on the interior side of the packaging bag. Next, both ends of the folded portion were heat-sealed with a heat sealer (a product of Tester Sangyo Co.), thereby preparing a 20 cm-square packaging bag that was open at one end. The appearance of the packaging bag thus prepared was excellent. The sealing strength of the two sealed ends was also excellent. Sealing conditions: seal bar temperature, 90 °C; sealing pressure, 2 kgf/cm<sup>2</sup>; and sealing time, 1 second (the size of the seal bar used was 10 x 300 mm.)

[0098] To evaluate heat resistance, a 300 g weight was placed inside the packaging bag thus prepared, which was then hung inside an air oven that was set at 60 °C and 80 °C test temperatures, and, twenty minutes later, the effect of the weight on the packaging bag was observed. The length of the packaging bag when it was hung was 20 cm. O was assigned when the sample showed no noticeable change (that is, the length of the bag was within 21 cm); X when the sample showed

considerable elongation and deformation or tore, causing the weight to drop (that is, the length of the bag was longer than 22 cm); and Δ when the sample was between these conditions. As a result, the packaging bag was found to show no deformation or tearing.

[0099] Haze value: The obtained film was evaluated by the same /11 method as the one used in Working Examples 1 through 5. The results are shown in Table 2. The biodegradability evaluation was carried out by the same method as the one used in Working Examples 1 through 5, with the packaging bag filled with food scraps as a specimen. The biodegradability was found to be excellent.

[0100] (Working Example 13) Using the lactic acid polymer (A) and an amorphous lactic acid polymer (B) specified in Table 2 as the base layer (I) and as the sealing layer (II), respectively, a 35 µm-thick laminate film in which the base layer (I) was 20 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Thereafter, this film was thermoset in an air oven at 100 °C for 10 minutes. Then, one end of the laminate film thus obtained was folded to form the bottom portion of a packaging bag, with the sealing layer disposed on the interior side of the packaging bag. Next, both ends of the folded portion were sealed by fuse sealing, thereby preparing a 20 cm-square packaging bag that was open at one end. The appearance of the packaging bag thus prepared was excellent. The sealing strength of the two sealed ends was also excellent.

Sealing condition: seal bar temperature, 300 °C.

Haze value: the obtained film was evaluated by the same method as the one used in Working Examples 1 through 5. The result is shown in Table 2.

[0101] The heat resistance evaluation was carried out in the same manner as in Working Example 12. As a result, at 60 °C and 80 °C test temperatures, the packaging bag showed no noticeable deformation or tearing; thus, its heat resistance was found to be excellent. The biodegradability evaluation was carried out in the same manner as in Working Example 12. As a result, the biodegradability was found to be excellent.

[0102] (Working Example 14) Using the lactic acid polymer (A) and an amorphous lactic acid polymer (B) specified in Table 2 as the base layer (I) and as the sealing layer (II), respectively, a 35 µm-thick laminate sheet in which the base layer (I) was 20 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Thereafter, this sheet was thermoset in an air oven at 100 °C for 10 minutes. Then, one end of the laminate film thus obtained was folded to form the bottom portion of a packaging bag, with the sealing layer disposed on the interior side of the packaging bag. Next, both ends of the folded portion were sealed by impulse sealing, thereby preparing a 20 cm-square packaging bag that was open at one end.

[0103] The appearance of the packaging bag thus prepared was excellent. The seal strength of the two sealed ends was also excellent. The sealing machine used here was a Polysealer manufactured by Fuji Co. The heat resistance evaluation was carried out in the same manner as in Working Example 12. As a result, at 60 °C and 80 °C test temperatures, the packaging bag showed no noticeable deformation or tearing. The biodegradability evaluation was carried out in the same manner as in Working Example 12. As a result, the biodegradability was found to be excellent.

[0104] (Working Example 15) Using the lactic acid polymer (A) and an amorphous lactic acid polymer (B) specified in Table 2 as the base layer (I) and as the sealing layer (II), respectively, a 115 µm-thick laminate sheet in which the base layer (I) was 100 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Thereafter, this film was thermoset in an air oven at 100 °C for 10 minutes. Then, the obtained laminate sheet was rolled up to form a cylinder, with the sealing layer disposed on the interior side of the case, and both ends of the sheet were overlapped and heat-sealed, thereby forming the lateral portion of a cylindrical case. The height of the cylinder was 10 cm, and the diameter thereof was 5 cm. The sealed portion on the lateral surface of the case thus prepared had a good appearance. The sealing strength was also excellent.

Sealing conditions: seal bar temperature, 90 °C; sealing pressure, 2 kgf/cm<sup>2</sup>; and sealing time, 1 second.

[0105] Evaluation of heat resistance: A cylindrical case thus prepared was positioned vertically inside an air oven that was set to a test temperature of 60 °C and another in an air oven at 80 °C and left standing for 20 minutes to evaluate the heat resistance. The samples showed no noticeable shrinkage, deformation, and so forth. The biodegradability evaluation was carried out by the same method as the one used in Working Examples 1 through 5, with the case filled with food scraps as a specimen. As a result, the biodegradability was found to be excellent.

[0106] (Working Example 16) Using the lactic acid polymer (A) and the amorphous lactic acid polymer (B) specified in Table 2 as the base layer (I) and as the sealing layer (II), respectively, a 265 µm-thick laminate sheet for vacuum forming use in which the base layer (I) was 250 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Similarly, a 35 µm thick laminate film for sealing use in which the base layer (I) was 20 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion. Thereafter, this film was thermoset in an air oven at 100 °C for 10 minutes.

[0107] The sheet was formed into a test-use lightweight container by vacuum forming with a cup mold that had a circular opening of 55 mm in diameter and a drawing ratio of 0.36 (female die). Here, the

sealing layer was disposed on the interior side of the container, and the flange of the molded product corresponding to the seal part was 3 mm in width.

Vacuum forming conditions: heater temperature, 400 °C; heating time, 10 seconds; mold temperature, 80 °C; and forming time: 30 seconds.

[0108] The heat resistance was evaluated by placing the cups thus obtained inside air ovens that were set at 60 °C and 80 °C and leaving them for 20 minutes. The samples showed no noticeable shrinkage, deformation, and the like at 60 °C, but slight deformation was observed at 80 °C. Evaluation of appearance (O: good, X: shrunk, and Δ: slightly deformed.) Next, the cup and the sealing-use film were heat-sealed by using an Autocup Sealer (a product of Sunrise System Co.) at a sealing temperature of 90 °C under a sealing pressure of 2 kgf/cm<sup>2</sup> for 1 second. The sealing layers of the cup and film served as the sealing faces. The lightweight container thus sealed showed a high sealing strength and good appearance at the sealed part.

[0109] The biodegradability evaluation was carried out by the same method as the one used in Working Examples 1 through 5, with the lightweight container filled with food scraps as a specimen. As a result, the biodegradability was found to be excellent.

[0110] (Working Examples 17 and 18) Using each lactic acid polymer (A) and each amorphous lactic acid polymer (B) specified in Table 3 as the base layer (I) and as the sealing layer (II), respectively, a 35 µm-thick laminate film in which the base layer (I)

was 20  $\mu\text{m}$  thick and the sealing layer (II) 15  $\mu\text{m}$  thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Thereafter, these films were thermoset in an air oven at 100 °C for 10 minutes. The following evaluations were carried out on the laminate /12 films thus obtained. The sealing strength, heat resistance, haze value, and biodegradability of the laminate films thus obtained were evaluated by the same methods as those used in Working Examples 1 through 5. The results are shown in Table 3.

[0111] Said laminate films had their sealing initiation temperature at about 80 °C and maintained a good sealing strength (500 gf/15 mm or above) at a temperature of 90 °C or higher. With respect to heat resistance, in the actual use tests performed with the use of weights, these films exhibited good heat resistance at 60 °C and 80 °C test temperatures. The minimum storage modulus ( $E'$ ) of each laminate film here was 1,300 kgf/cm<sup>2</sup> in Working Example 17 and 1,000 kgf/cm<sup>2</sup> in Working Example 18. The transparency and biodegradability of the films were excellent. Incidentally, the sealing temperatures were shown next to the sealing strength in Tables 1 through 4.

[0112]

[Table 1]

実施例 (a)		1	2	3	4	5	6	7	8
(b) 乳酸系ポリマー (A)	P1	P2	P3	P4	P5	P6	P7	P8	P1
(c) 熔点 [℃]	163	176	168	162	162	163	162	163	163
(d) 結晶化温度 [℃]	110	110	108	93	73	108	93	110	110
乳酸系ポリマー (B)	P6	P7	P8	P9	P9	P8	P8	P8	P8
(e) 軟化温度 [℃]	92	52	46	37	37	46	37	46	46
厚み (f) [μm]	35	35	35	35	35	35	35	35	35
ヘイズ (g) [%]	13	18	10	19	14	10	19	1.0	1.0
(h) (i) 热 耐 热 性	60℃	○	○	○	○	○	○	○	○
	80℃	○	○	○	○	○	○	○	○
(j) 生分解性 (j)		○	○	○	○	○	○	○	○
(k) (l) 静 電 強 度 [kgf/cm²]	80℃	80	70	30	600	600	10	10	0
	90℃	1400	1350	1400	1400	1350	170	160	300
(x)	100℃	1700	1750	1600	1600	1650	180	170	1600
	120℃	2000	1900	1900	1650	1650	180	170	1500
	140℃	3000	1900	2000	1650	1700	180	170	1700

Key: a) working examples; b) lactic acid polymer (A); c) melting point; d) crystallization temperature; e) softening temperature of lactic acid polymer (B); f) thickness; g) haze; h) heat resistance; i) actual use test; j) biodegradability; k) sealing strength.

[0113]

[Table 2]

実施例(a)		9	10	11	12	13	14	15	16
(B) 乳酸系ポリマー(A) 融点(c) [℃] 結晶化温度(d) [℃]	P5	P4	P1	P2	P3	P4	P2	P3	
	162	162	163	176	166	162	176	166	
	78	98	110	110	108	93	110	108	
乳酸系ポリマー(B) 軟化温度(e) [℃]	P9	P9	P6	P7	P8	P9	P7	P8	
	57	57	62	52	46	57	52	46	
厚み(f) [μm] ヘイズ(g) [%]	35	50	35	35	35	35	—	—	
	L1	15	18	18	10	21	—	—	
(h) 耐熱性 実試験	60°C	○	○	○	○	○	○	○	
	80°C	△	○	△	○	○	○	△	
E' [kN/cm²]		600	1100	780	1600	1300	1100	1500	—
生分解性(j)		○	○	○	○	○	○	○	○
(k) 引張強度 [kgf/15mm]	8.0°C	0	400	80					
	9.0°C	600	1350	1400					
	10.0°C	1850	1900	1700					
	12.0°C	1800	2300	2000					
	14.0°C	1900	2350	2000					

Key: a) working examples; b) lactic acid polymer (A); c) melting point; d) crystallization temperature; e) softening temperature of lactic acid polymer (B); f) thickness; g) haze; h) heat resistance; i) actual use test; j) biodegradability; k) sealing strength.

[0114]

[Table 3]

実施例(a)		17	18
(b) 乳酸系ポリマー(A)	P1	P4	
融点(c) [℃]	103	102	
結晶化温度 [℃] (d)	110	98	
乳酸系ポリマー(B) 軟化温度 (e) [℃]	P10	P11	
厚み(f) [μm]	35	35	
ヘイズ(g) [%]	13	19	
(h) (i) 耐熱性 実試験	60℃	○	○
	80℃	○	○
	E' [kgf/cm <sup>2</sup> ]	1300	1100
生分解性(h)		○	○
引張強度 [kgf/15mm]	80℃ 90℃	40 600	200 700
(k)	100℃ 120℃ 140℃	800 1000 1000	800 800 800

Key: a) working examples; b) lactic acid polymer (A); c) melting point; d) crystallization temperature; e) softening temperature of lactic acid polymer (B); f) thickness; g) haze; h) heat resistance; i) actual use test; j) biodegradability; k) sealing strength.

[0115] (Comparative Examples 1 and 2) Using each amorphous lactic acid polymer (B) and each lactic acid polymer (A) specified in Table 4 as the base layer (I) and as the sealing layer (II), respectively, a 35 μm-thick laminate film in which the base layer (I) was 20 μm thick and the sealing layer (II) 15 μm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.), and the film thus formed was thermoset in an air oven at 100 °C for 10 minutes. The sealing strength, heat resistance, haze value, and biodegradability of the laminate films thus obtained were evaluated by the same methods as

those used in Working Examples 1 through 5. The results are shown in Table 4. With respect to heat resistance, in the actual use tests performed with the use of weights, each laminate film exhibited no problem at the 60 °C and 80 °C test temperatures. The minimum storage modulus (E') of each laminate film here was 900 kgf/cm<sup>2</sup> or above, but no sealing strength was achieved.

[0116] (Comparative Examples 3 and 4) Using each amorphous lactic acid polymer (B) and each lactic acid polymer (A) specified in Table 4 as the base layer (I) and as the sealing layer (II), respectively, a 140 µm-thick laminate sheet in which the base layer (I) was 80 µm thick and the sealing layer (II) 60 µm thick was formed by extrusion. Next, the obtained film was stretched by using a single-engine biaxial stretching machine (a product of Iwamoto Seisakusho Co.) under the following conditions: stretching temperature, 65 °C; preheating time, 5 minutes; stretching rate, 100 %/minute; stretching ratio, 2 X 2 (length X width); and area draw ratio: 4, thereby preparing a drawn laminate film of 35 µm in thickness. This film was fixed in a 30 cm-square frame and thermoset in an air oven at 100 °C for 20 seconds. The sealing strength, heat resistance, haze value, and biodegradability of the laminate films thus obtained were evaluated by the same methods as those used in Working Examples 1 through 5. The results are shown in Table 4.

[0117] With respect to heat resistance, in the actual use tests performed with the use of weights, each film exhibited no problem at a

test temperature of 60 °C , but it showed elongation at 80 °C. The minimum storage modulus (E') of each laminate film here was 600 kgf/cm<sup>2</sup> in Comparative Example 3 and 500 kgf/cm<sup>2</sup> in Comparative Example 4. However, no sealing strength was achieved.

[0118] (Comparative Example 5) Using the amorphous lactic acid polymer (B) and lactic acid polymer (A) specified in Table 4 as the base layer (I) and as the sealing layer (II), respectively, two kinds of single-layer films, each having a thickness of 25 µm, were formed by extrusion with the use of an extruder (a product of Tanabe Plastics Co.) Next, only the single-layer film composed of the lactic acid polymer (B) was thermoset in an air oven at 100 °C for 10 minutes. Thereafter, a 30 % gelatin [sic] was applied to one surface of each of the two films thus obtained, which were then adhered to each other under pressure of 2 kgf/cm<sup>2</sup> and dried.

[0119] Thus, a laminate film of about 50 µm in thickness having a good appearance was obtained. The sealing strength, heat resistance, haze value, and biodegradability of the laminate film thus obtained were evaluated by the same methods as those used in Working Examples 1 through 5. The results are shown in Table 4.

In the actual use tests performed with the use of weights to evaluate heat resistance, the film exhibited deformation caused by considerable elongation at both 60 °C and 80 °C test temperatures. The minimum storage modulus (E') of the laminate film was more than 900 kgf/cm<sup>2</sup>, namely, 1100 kgf/cm<sup>2</sup>, but no sealing strength was achieved.

[0120] (Comparative Example 6) Using the lactic acid polymer (A) and an amorphous lactic acid polymer (B) specified in Table 4 as the base layer (I) and as the sealing layer (II), respectively, a 35 µm-thick laminate film in which the base layer (I) was 20 µm thick and the sealing layer (II) 15 µm thick was formed by extrusion with a coextruder (a product of Tanabe Plastics Co.) Thereafter, the heat resistance and haze value of the laminate film obtained without implementing thermosetting were evaluated by the same methods as those used in Working Examples 1 through 5. The results are shown in Table 4. When the heat resistance of the laminate film thus prepared was tested, it tore at 60 °C and 80 °C test temperatures in actual use tests performed with the use of weights. The minimum storage modulus (E') of the laminate film here was 0 kgf/cm<sup>2</sup>; thus, the film had no heat resistance.

[0121] (Comparative Example 7) Using the lactic acid polymer (A) specified in Table 4, a 35 µm-thick, single-layer film was formed by extrusion with an extruder (a product of Tanabe Plastics Co.), and the film was subsequently thermoset in an air oven at 100 °C for 10 minutes. The sealing strength, heat resistance, and haze value of the single-layer film thus obtained were evaluated by the same methods as those used in Working Examples 1 through 5. The results are shown in Table 4. The film had no heat-sealing strength.

[0122] (Comparative Example 8) Using the amorphous lactic acid polymer (B) specified in Table 4, a 35 µm-thick, single-layer film was

formed by extrusion with an extruder (a product of Tanabe Plastics Co.), and the film was subsequently thermoset in an air oven at 100 °C for 10 minutes. The heat resistance, haze value, and biodegradability of the single-layer film thus obtained were evaluated by the same methods as those used in Working Examples 1 through 5. The test results are shown in Table 4. When the heat resistance of the laminate [sic] film thus prepared was tested, it tore at 60 °C and 80 °C test temperatures in actual use tests performed with the use of weights. The minimum storage modulus ( $E'$ ) of the laminate [sic] film here was 0 kgf/cm<sup>2</sup>; thus, the film had no heat resistance.

[0123]

[Table 4]

比較例(a)		1	2	3	4	5	6	7	8	
(b)										
乳酸系ポリマー(A)		P1	P3	P2	P5	P4	P1	P2	...	
融点(c) [°C]	163	168	176	162	162	163	176	-	-	
結晶化度(d) [°C]	110	108	110	73	93	110	110	-	-	
(c)										
乳酸系ポリマー(B)		P6	P8	P7	P9	P9	P7	...	P8	
軟化温度(e) [°C]	52	46	46	57	57	52	-	-	46	
厚み(f) [μm]	35	35	35	35	50	36	35	35	35	
ヘイズ(g) [%]	5	7	1.0	1.1	9	13	15	10	10	
(d)										
耐熱性(h)	(i)	60°C	○	○	○	○	×	×	○	×
		80°C	○	○	△	△	×	×	○	×
$E'$ [kgf/cm <sup>2</sup> ]										
生分解性(j)		○	○	○	○	○	○	○	○	
(k)		80°C [kgf/cm <sup>2</sup> /15min]	0	0	0	0	0	-	0	-
		90°C	0	0	0	0	0	-	0	-
		100°C	0	0	0	0	0	-	0	-
		120°C	0	0	0	0	0	-	0	-
		140°C	0	0	0	0	0	-	0	-

Key: a) comparative examples; b) lactic acid polymer (A); c) melting point; d) crystallization temperature; e) softening temperature of lactic acid polymer (B); f) thickness; g) haze; h) heat resistance; i) actual use test; j) biodegradability; k) sealing strength.

[0124]

[Effects of the Invention] The present invention can provide heat-sealable lactic acid polymer laminates that have a heat resistance of 60°C or higher, high sealing strength, and good biodegradability and that are useful for various films, sheets, packaging containers, etc.